PREPARATION OF POLYMERIC ALUMINIUM FERRIC CHLORIDE FROM BAUXITE TAILINGS

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Abstract

Bauxite tailings are the main solid wastes in the ore dressing process. The Al\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} contents in bauxite tailings can reach 50\% and 13\% respectively. The present study proposed a feasible method to use bauxite tailings to prepare polymeric aluminium ferric chloride (PAFC), a new composite inorganic polymer for water purification. Bauxite tailings roasted reacted with hydrochloric acid under air, pickle liquor which mainly contains Fe\textsuperscript{3+}, Al\textsuperscript{3+} was generated, then calcium aluminate was used to adjust pH value and the basicity of the pickle liquor, the PAFC was subsequently prepared after the polymerization process. The optimal synthesizing parameters for the preparation of PAFC obtained were as follows: the concentration of hydrochloric acid of 24 wt\%, ratio of hydrochloric acid to bauxite tailings of 6:1, temperature of 90\(^\circ\)C, leaching time of 2.5 hours, ratio of pickle liquor to calcium aluminate of 12:1, polymerization temperature of 90\(^\circ\)C and polymerization time of about 3 hours. The basicity of PAFC was higher than 68\%, the sum concentration of Al\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} was beyond 12.5\%. The results of flocculation tests indicate that the PAFC has a better performance of removing the turbidity of wastewater compared to PAC, and PAFC prepared by bauxite tailings is a kind of high quality flocculants.

Keywords: Bauxite tailings; PAFC; Hydrochloric acid leaching; Calcium aluminate.

1. Introduction

Bauxite tailings are one of the main solid wastes generated in the flotation-Bayer process which uses low grade bauxite ore to produce alumina in China [1]. About 30wt\% bauxite tailings are produced in every one ton Al\textsubscript{2}O\textsubscript{3} producing. At present, most of them are deposited on land surface without any utilization, which pollutes environment seriously. In recent years, much attention has been paid to utilize bauxite tailings to produce refractory, construction material, absorbent material and alloy material [2-5]. The main chemical components of bauxite tailings include Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, and K\textsubscript{2}O [6]. The content of alumina and ferric oxide in bauxite tailings are as high as 50\% and 13\%, respectively, while Fe\textsuperscript{3+} salts and Al\textsuperscript{3+} salts are most commonly used as coagulation in water treatment. Hence, according to the chemical composition of bauxite tailing, it is suitable for the production of polymeric aluminium ferric chloride.

Polymeric aluminum ferric chloride (PAFC in abbreviation) is a new inorganic compound coagulant which is widely used in water purification. The main chemical components in PAFC are Fe\textsuperscript{3+}, Al\textsuperscript{3+}, Cl\textsuperscript{-} and OH\textsuperscript{-}. It has been developed from pre-hydrolyzing AlCl\textsubscript{3} and FeCl\textsubscript{3} by alkali [7]. It has a higher capacity on flocculating and condensation, and could produce large floc aggregates which can be removed from the waste water in subsequent filtration processes [8]. Raw Material for synthesis of PAFC are various, Genli Wang prepared PAFC by bauxite, but waste acid containing Fe was needed to increase the iron content of PAFC [9]. Shihua Pang prepared PAFC by red mud, but it is low content of Al [10]. Other material like mineral (such as gibbsite, bauxite, hematite), pure reagent (such as aluminium chloride, pure ferric chloride, aluminium hydroxide) and industrial wastes (such as blast furnace dust, gangue, hydrochloric pickle liquor) [11-13] for preparing PAFC are either high-cost or low content of Al and Fe. Bauxite tailings are a kind of solid wastes which contain large amounts of Al and Fe (up to 49\% and 13\% respectively), so that it is reasonable to suggest that if the high cost of raw materials are replaced by bauxite tailings, it may not only reduce the cost for preparing PAFC, but also be an effective way to utilize bauxite tailings. However, relative works have seldom been reported.

In this paper, a feasibility of the preparation route from bauxite tailings to polymeric aluminium ferric chloride (PAFC) was investigated. The composition of PAFC was characterized, and the flocculation performance of PAFC was investigated as well.
2. Experiment
2.1 Material and methods

The bauxite tailings (Zhengzhou, Henan Province, China), hydrochloric acid (analytical grade, 37 wt%) and calcium aluminate (Gongyi, Henan Province, China), were chosen as raw materials for the preparation of PAFC. Kaolin (Lingshou, Hebei Province, China), Polymeric aluminium chloride (PAC in abbreviation, from Gongyi, Henan Province, China), NaOH and HCl (analytical grade) were chosen as materials for the flocculation performance test of PAFC. All aqueous solutions in this study were prepared with de-ionized water.

The chemical composition of bauxite tailings and calcium aluminate were shown in Table 1. The X-ray diffraction pattern of bauxite tailings were shown in Figure 1. It was observed that Al₂O₃, SiO₂, Fe₂O₃, TiO₂, K₂O had constituted the major main chemical compositions of bauxite tailings, while its main mineral compositions were diaspore, kaolinite, with a small amount of hematite, anatase, etc.

The PAC was provided by Huaming Chemical material Co., in Gongyi, Henan Province, China. It is a kind of buff liquid produce, the content of Al₂O₃ in PAC is higher than 8%, and basicity of PAC is higher than 70%.

The preparation of PAFC consists of 2 main steps, hydrochloric acid leaching and polymerization process.

The objective of hydrochloric acid leaching process is to dissolve Al₂O₃ and Fe₂O₃ in bauxite tailings as much as possible. In this process, bauxite tailings were firstly shattered, grinded and roasted. The preheated bauxite tailings were directly reacted with hydrochloric acid in the air. Aluminum oxide and ferric oxide were dissolved in hydrochloric acid gradually. At the end of this process, the liquor mainly contained AlCl₃, FeCl₃ and residual acid, while the solid mainly contained SiO₂. After the solid-liquid separation, pickle liquor which mainly contained Al³⁺, Fe³⁺ and residual acid was generated.

The concentration of hydrochloric acid, the ratio of hydrochloric acid to bauxite tailings, the leaching temperature and the leaching time affected the dissolution ratio of Al₂O₃ and Fe₂O₃ in bauxite tailings. Therefore, these 4 parameters were detailed investigated and their synthesis composition were shown in Table 2.

The next process was followed by polymerization process. Al³⁺ and Fe³⁺ in pickle

| Table 1. Chemical compositions of bauxite tailings and calcium aluminate (wt%). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Al₂O₃ | SiO₂ | Fe₂O₃ | TiO₂ | K₂O | CaO | Na₂O | MgO | Ig |
| Bauxite tailings| 49.87 | 22.45 | 13.1  | 2.61 | 2.25 | 0.41 | 0.23 | -   | 11.5 |
| Calcium aluminate| 58.51 | -    | 3.96  | 0.42 | -   | 26.72 | 0.11 | -   | -   |

Figure 1. XRD pattern of bauxite tailings.
liquor were expected to be hydrolyzed in this process and then the macromolecule hydroxyl polymer of Al and Fe would generate. At the beginning of polymerization, Al$^{3+}$ and Fe$^{3+}$ in pickle liquor were exist as Al(H$_2$O)$_6$$^{3+}$ and Fe(H$_2$O)$_6$$^{3+}$, they could not hydrolyze and polymerize in acidic conditions cause of residual acid. Calcium aluminate was added into the pickle liquor to neutralize residual acid and raise the pH value of the pickle liquor. With increased the pH value, Al(H$_2$O)$_6$$^{3+}$ and Fe(H$_2$O)$_6$$^{3+}$ were gradually hydrolyzed, polymerized and copolymerized. After polymerization and copolymerization reaction reached equilibrium, most Al and Fe existed as polymeric aluminium ferric chloride (PAFC), PAFC was then successfully synthesized.

Basicity (B) is the most characterizations to represent the degree of polymerization of PAFC. It represents the averages quantity of hydroxyl ligands combined with metal atoms. The higher the basicity is, the higher the degree of polymerization is, the better the flocculation performance of PAFC would be.

Basicity of PAFC was deeply depended on the ratio of calcium aluminate to pickle liquor, the polymerization reaction time and the polymerization reaction temperature, respectively. Hence, the relationship between the basicity of PAFC and the polymerization parameters were detailed investigated and their synthesis composition were shown in Table 3.

### Table 2. The synthesis parameters in hydrochloric acid leaching process.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid concentration ($C_1$)</td>
<td>12%, 16%, 20%, 24%, 28%</td>
</tr>
<tr>
<td>Ratio of hydrochloric acid to bauxite tailings (wt/wt) ($R_1$)</td>
<td>4:1, 5:1, 6:1, 7:1, 8:1</td>
</tr>
<tr>
<td>Acid leaching temperature ($T_1$)</td>
<td>75°C, 80°C, 85°C, 90°C, 95°C</td>
</tr>
<tr>
<td>Acid leaching time ($H_1$)</td>
<td>1h, 1.5h, 2h, 2.5h, 3h</td>
</tr>
</tbody>
</table>

### Table 3. The Parameters in polymerization process.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of pickle liquor to calcium aluminate ($R_p$)</td>
<td>60:6, 60:5, 60:4, 60:3</td>
</tr>
<tr>
<td>Polymerization temperature ($T_p$)</td>
<td>70°C, 80°C, 90°C, 100°C</td>
</tr>
<tr>
<td>Polymerization time ($H_p$)</td>
<td>2h, 3h, 4h, 5h</td>
</tr>
</tbody>
</table>

### 2.3 Flocculation test

Turbidity removal is the most characterizations of the performance of PAFC in flocculation test. Turbidity removal tests were performed in kaolin turbid liquid. The kaolin turbid liquid was prepared by adding 100mg kaolin to 1.0L deionized water. The performance of PAFC were investigated compared with PAC which is widely applied as a traditional flocculant. In the turbidity removal test, varied volumes of PAFC (PAC) were loaded into 1.0L turbid liquid with varied pH value, respectively. Then the mixture was stirred under a rotate speed of 300min$^{-1}$ for 3min, and then 30min$^{-1}$ for 7min, after it was deposited and kept static for 10min. Finally, the water below surface’s 10cm was fetched to perform turbidity removal test by turbid meter.

The Turbidity was measured under varied dose of PAFC and PAC (DP), pH value of kaolin turbid water (pH$_k$), respectively. Their synthesis composition was shown in Table 4.

### Table 4. The Parameters in Turbidity removal test.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose of PAFC and PAC (D$_p$)</td>
<td>2.4, 6,…, 12 ml</td>
</tr>
<tr>
<td>pH value of kaolin turbid water (pH$_k$)</td>
<td>2, 4, 6,…, 12</td>
</tr>
</tbody>
</table>

### 2.4 Chemical and phase analysis

The mineral composition of bauxite tailings was measured by X-Ray Diffract meter (XRD) with Cu K radiation in the range 10-100° (2θ) at a scan rate of 5°min$^{-1}$ supplied from Japan. The pH value of pickle liquor was measured by pH meter supplied by PHS-29A from Shanghai, China.

The dissolution ratio of Al$_2$O$_3$ (Dis$_A$) and Fe$_2$O$_3$ (Dis$_F$) of bauxite tailings were calculated as shown in equation (1) and (2).

$$Dis_A = \frac{Con_{AB} - Con_{Al}}{Con_{Al}}$$  \(_{(1)}\)

$$Dis_F = \frac{Con_{FB} - Con_{Fl}}{Con_{Fl}}$$  \(_{(2)}\)

In the equation (1), Con$_{AB}$ (Con$_{FB}$) was the content of Al$_2$O$_3$ (Fe$_2$O$_3$) in bauxite tailings. Con$_{Al}$ (Con$_{Fl}$) was content of Al$_2$O$_3$ (Fe$_2$O$_3$) in pickle liquor, which was measured by ICP (Inductive Coupled Plasma Emission Spectrometer).

Basicity (B) of PAFC was measured as equation shown in Equal. (3) [14].

$$B = \frac{[OH^-]}{3(Fe_T + Al_T)} \times 100\%$$  \(_{(3)}\)

In the equation (3), [OH$^-$] were the mole amounts of hydroxyl in pickle liquor after the culate aluminate was hydrolyzed. Fe$_T$ and Al$_T$ were the mole
amounts Fe$^{3+}$ and Al$^{3+}$ in pickle liquor, it was measured by ICP.

Turbidity of kaolin turbid water was measured by turbid meter WGZ-800 supplied from Shanghai, China.

3. Results and Discussions

3.1 Acid leaching process

Preparation of PAFC began with the acid leaching process. The preheated bauxite tailings were directly reacted with hydrochloric acid. Al$_2$O$_3$ and Fe$_2$O$_3$ were dissolved in hydrochloric acid, and pickle liquor which mainly contained Al$^{3+}$ and Fe$^{3+}$ was generated. The main reactions in this process were shown in equation (4) - (5).

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 6\text{HCl} & \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O} \quad (4) \\
\text{Fe}_2\text{O}_3 + 6\text{HCl} & \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \quad (5)
\end{align*}
\]

Al$^{3+}$ and Fe$^{3+}$ in pickle liquor were the most important components of PAFC. High contents of Al$^{3+}$ and Fe$^{3+}$ will enhance the polymerization in the next process. Hence, higher dissolution ratios of Al$_2$O$_3$ and Fe$_2$O$_3$ in bauxite tailings were expected. In order to increase the dissolution ratio of Al$_2$O$_3$ and Fe$_2$O$_3$, the parameters of acid leaching process were detailed investigated, namely, the concentration of hydrochloric acid ($C_L$), ratio of hydrochloric acid to bauxite tailings ($R_L$), leaching temperature ($T_L$) and leaching time ($H_L$).

The dissolution ratios of Al$_2$O$_3$ and Fe$_2$O$_3$ in bauxite tailings depended on each parameter were shown in Figure 2 to Figure 5.

From Figure 2 to Figure 5, it was shown that the dissolution ratio of Al$_2$O$_3$ and Fe$_2$O$_3$ in bauxite tailings increased along with the increase of the concentration of hydrochloric acid ($C_L$), ratio of hydrochloric acid to
bauxite tailings (RL), leaching temperature (TL) and leaching time (HL). Because as the increase of CL and TL, kinetic condition of acid leaching process improved, the dissolution rate increased therewith. However, too high CL and TL would lead to the volatilization of hydrochloric acid. So, CL of 24wt% and TL of 90°C were selected as the best parameters. With the increase of RL, surplus acid was increased which was beneficial to the dissolution of Al₂O₃ and Fe₂O₃. But exorbitant RL would generate much residual acid in pickle liquor which would consume large amounts of calcium aluminate to neutralize in the next process. Therefore, RL of 6:1 was chosen as the optimal parameter. With the increase of HL, leaching reaction continued, but the reaction reached equilibrium at HL of 2.5 hours, so it was selected as the best parameter. Finally, according to the analysis above, CL of 24wt%, RL of 6:1, TL of 90°C and HL of 2.5 hours were the optimal parameters of the acid leaching process, the dissolution ratio of Al₂O₃ and Fe₂O₃ reached 62.4% and 93.5% under this circumstances, respectively.

3.2 Polymerization process

After the acid leaching process, pickle liquor mainly contained Al³⁺, Fe⁶⁺ and residual hydrochloric acid. Al³⁺ and Fe⁶⁺ existed as Al(H₂O)₆⁺ and Fe(H₂O)₆⁺. They couldn’t hydrolyze under a very low pH value. Then, calcium aluminate (CaO·Al₂O₃, CaO·2Al₂O₃) was added into the pickle liquor gradually to neutralize the residual acid and raise the pH value of pickle liquor. Calcium aluminate was mainly made up of alkaline oxides as shown in table 1, once it was added into the pickle liquor, reaction immediately occurred as equation (6) and (7) showing.

\[
\begin{align*}
\text{CaO} \cdot \text{Al}_2\text{O}_3 + 8\text{HCl} & \rightarrow \text{CaCl}_2 + 2\text{AlCl}_3 + 4\text{H}_2\text{O} \\
\text{CaO} \cdot 2\text{Al}_2\text{O}_3 + 14\text{HCl} & \rightarrow \text{CaCl}_2 + 4\text{AlCl}_3 + 7\text{H}_2\text{O}
\end{align*}
\]

With the progressing of reaction, residual hydrochloric acid was gradually neutralized, the content of Al³⁺ in pickle liquor slowly increased, and pH value of pickle liquor increased too, Al(H₂O)⁶⁺ and Fe(H₂O)⁶⁺ hydrolyzed gradually as shown in equation (8) - (11). Also, polymer of Al and Fe were generated gradually by the polymerization and copolymerization as shown in equation (12) - (14) [14].

\[
\begin{align*}
2\text{FeCl}_3 + n\text{H}_2\text{O} & \rightarrow \text{Fe}_n(\text{OH})_{3n-}\text{Cl}_{3n-} + n\text{Cl}^- + n\text{H}^+ \\
2\text{AlCl}_3 + n\text{H}_2\text{O} & \rightarrow \text{Al}_n(\text{OH})_{3n-}\text{Cl}_{3n-} + n\text{Cl}^- + n\text{H}^+
\end{align*}
\]

At the end of the polymerization process, most Al and Fe exited as polymeric aluminium ferric chloride, PAFC was successfully synthesized. Basicity (B) is the most characterizations representing the degree of polymerization of PAFC. Basicity signifies the average quantity of hydroxyl ligands combined with Al and Fe atoms. Higher basicity will enhance the flocculation performance, but the PAFC will precipitate easily when the basicity is higher than about 80%. Therefore within the approved basicity, higher basicity will achieve a better flocculation performance of PAFC. In the condition that PAFC was stable without precipitation, the highest basicity was reported to be around 70% [15].

The ratio of pickle liquor to calcium aluminate (RL), polymerization temperature (TP) and polymerization time (HP) affected the basicity of PAFC, therefore, these 3 parameters were investigated as shown in Figure 6 to Figure 8.
From Figure 6, it was shown that, with the decrease of $R_P$, the dosage of calcium aluminate added into pickle liquor increased. Therefore the hydroxyl generated by hydrolyzing of calcium aluminate increased, as a result the basicity of pickle liquor increased. While the optimum basicity of PAFC is about 70% according references [15], So $R_P$ of 12:1 was chosen to be the optimal parameter. From Figure 7, it was shown that the basicity of pickle liquor was increased with the increase of polymerization temperature ($T_P$). That’s because, with the increase of $T_P$, kinetic condition of polymerization process improved, therefore the dissolution rate of calcium aluminate and polymerization rate of PAFC increased, so the basicity increased. However as the $T_P$ is 90 °C, basicity reached a maximum, exorbitant $T_P$ would lead to the evaporation of liquid which was useless to the polymerization process. So $T_P$ of 90 °C was selected to be the best parameter.

Figure 8, it showed that with the increase of $H_P$, the basicity of pickle liquor was increased. Because, as $H_P$ increased, the dissolution ratio of calcium aluminate and polymerization ratio of PAFC increased. However, the reaction reached equilibrium as polymerization time was 3 hours. So $H_P$ of 3 hours was chosen to be the optimal parameter.

Finally, according to the analysis above, $R_P$ of 12:1, $T_P$ of 90 °C and $H_P$ of 3 hours were the optimal parameters of polymerization process.

PAFC was successfully synthesized after the polymerization process under the optimal synthesis parameters. The basicity of PAFC was higher than 68%. According to the ICP measurement, the sum concentration of Al$_2$O$_3$ and Fe$_2$O$_3$ was beyond 12.5% (the concentration of Al$^{3+}$ and Fe$^{3+}$ in the pickle liquor).

### 3.3 Flocculation test

Turbidity removal test was carried out in kaolin turbid liquid. The pH value and turbidity of the kaolin turbid liquid were 7.2 and 130NTU, respectively. Dose of PAFC and PAC ($D_P$) affected the performance of flocculation test. Also, pH value of kaolin turbid liquid ($pH_k$) was an important factor for the turbidity removal test as well. The turbidity removal performance of PAFC and PAC under varied $D_P$ and pH$_k$ were investigated as shown in Figure 9 and Figure 10.

As shown in Figure 9, in the range of dosage, the turbidity removal ratios of PAFC were evidently higher than that of PAC. Turbidity removal ratios reached about 80% as the dosage of PAFC was around 6ml·L$^{-1}$, compared with PAC of 8 ml·L$^{-1}$. It proved PAFC was more effective than PAC on turbidity removal test.
From Figure 10, it was shown that the turbidity removal ratio of PAFC and PAC both increased as pH value of turbid liquid increased from 2 to 8, and both slightly decreased as pH value increased from 8 to 12. Therefore, too high pH value of turbid liquid was not conducive to the coagulant efficiency, the optimal pH value for the PAFC flocculation performance was about 8. In the range of pH value of turbid liquid researched, basically, turbidity removal ratio of PAFC was higher than that of PAC.

According to the flocculation test results, it indicates that PAFC prepared by bauxite tailings had an excellent flocculation performance, and it was more effective than that of PAC.

4. Conclusions

PAFC was successfully synthesized from bauxite tailing in the present study, and the synthesizing parameters were investigated. The optimal synthesizing parameters attained include: the concentration of hydrochloric acid of 24 wt%, ratio of hydrochloric acid to bauxite tailings of 6:1, temperature of 90°C, leaching time of 2.5 hours, ratio of pickle liquor to calcium aluminate of 12:1, polymerization temperature of 90°C and polymerization time of about 3 hours respectively. The basicity of PAFC is higher than 68%, the sum concentration of Al2O3 and Fe2O3 was beyond 12.5%. According to flocculation tests, it indicated that the PAFC has a better performance of removing the turbidity of wastewater compared to the PAC. PAFC prepared by bauxite tailings is a kind of high quality flocculants.

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References